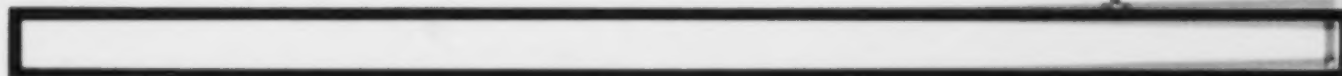


Fly Ash Concentrations in Philadelphia
Aerosol Determined by Electron
Microscopy (Journal Version)

(U.S.) Environmental Protection Agency
Research Triangle Park, NC

1988



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FLY ASH CONCENTRATIONS IN PHILADELPHIA AEROSOL DETERMINED BY ELECTRON MICROSCOPY

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Abstract. In a study to differentiate between coal-fly ash and minerals in the atmosphere, samples were collected on Nuclepore filters in dichotomous samplers and analyzed by scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry. The samples included ambient aerosol from two sites, resuspended soil, and emissions from coal- and oil-fired power plants in the Philadelphia area. Fly ash and minerals were identified by observing high abundances of Al, Si, K, Ca, Ti, and Fe in individual particles, and their mass concentrations were estimated from measured dimensions and an assumed density. Fly ash was distinguished from minerals by morphology. Sulfate was the major component of the fine fraction ($< 2.5 \mu\text{m}$ aerodynamic dia.). Crustal matter concentrations in the fine fraction estimated by SEM ranged from 40 to 300 ng m^{-3} , and fly ash accounted for 7 to 62% of the crustal matter. In the coarse fraction (2.5 to 10 μm), minerals were the predominant component and ranged in concentration from 500 to 6000 ng m^{-3} . Fly ash accounted for 0 to 16% of the crustal matter; the typical amount was 6%. Other less abundant coarse particles included botanical matter and industrial source emissions. Coarse fraction crustal matter estimated from x-ray fluorescence elemental data agreed well with that based on electron microscopy.

1. Introduction

Receptor models have been developed to identify emission sources that contribute to concentrations of particles in the atmosphere. The models are based on comparing the chemical compositions of ambient aerosol samples and source emissions. The chemical mass balance (CMB) type of receptor model requires that the compositions of source emissions not be collinear (Henry *et al.*, 1984). Sources with similar chemical compositions are collinear and cannot be resolved reliably by CMB. For example, fly ash and soil particles have similar compositions within the crustal category. Both contain mainly silicates of Al and varying concentrations of Fe and Ca. It is important to be able to resolve them because the crustal component constitutes a large fraction of coarse particles in the atmosphere.

The purpose of the present study is to explore the feasibility of using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) to distinguish coal- and oil-fly ash from minerals. The study is based on SEM-EDX analysis of ambient aerosol, resuspended soil, and emissions from coal- and oil-fired power plants in the Philadelphia area.

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2. Measurements

Ambient aerosol samples were collected during summer, 1982, in the Philadelphia area at three sites (Figure 1) along the line of prevailing winds (Dzubay *et al.*, 1988). (a) The site at North Airport is northeast of downtown Philadelphia in a residential area with some light industries where fairly large areas are covered with vegetation. (b) The Camden site is at the Institute for Medical Research in Camden, New Jersey, in a residential-commercial area near industrial sources along the Delaware River. (c) The Clarksboro site is in a rural, agricultural area south of Philadelphia. A detailed description of the sampling sites is given by Core (1982). Over 50 12-hr ambient samples were collected at each site.

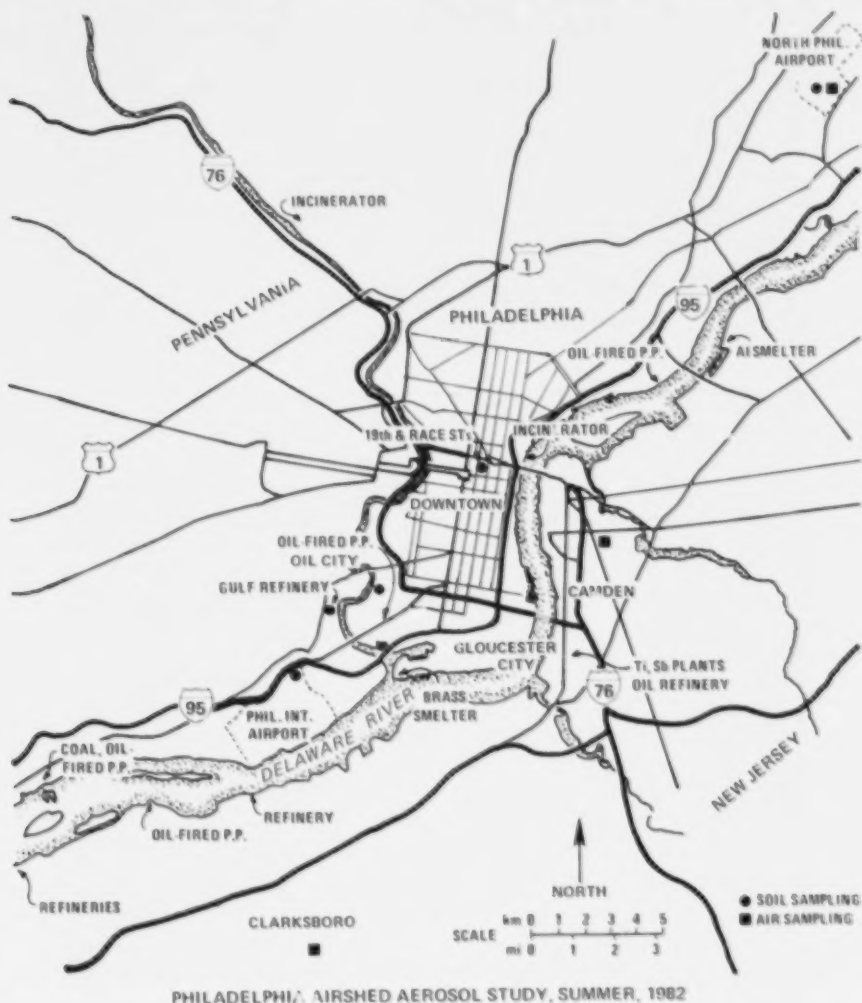
Sources sampled were oil- and coal-fired power plants, a municipal refuse incinerator, a refinery, an aluminum furnace, and an antimony roasting plant at locations indicated in Figure 1. Emissions from power plants were collected in a sampling train consisting of a stack probe, a dilution chamber which cooled the hot stack gases to the ambient level, and a dichotomous sampler (Olmez *et al.*, 1986). Soil samples from several sites (see Figure 1) in the Philadelphia area were collected at depths of 0.2 to 2 cm. In the laboratory, particles larger than 300 μm were removed by a sieve, and the remaining smaller ones were resuspended in a fluidized bed aerosol generator (Batterman *et al.*, 1987).

All source, resuspended soil, and ambient samples were collected by dichotomous samplers in two size fractions: fine ($< 2.5 \mu\text{m}$ aerodynamic diameter) and coarse (2.5 to 10 μm). Parallel samples were collected on 0.3- μm pore size Nuclepore filters and 2- μm Teflon filters. Soil samples on Teflon filters were analyzed for mass by β -gauge and bulk composition by X-ray fluorescence (XRF) (Battermann *et al.*, 1987). Ambient and source samples were analyzed for bulk composition by β -gauge, instrumental neutron activation, and XRF (Dzubay *et al.*, 1988; Olmez *et al.*, 1986). Individual particles on Nuclepore filters were analyzed by light microscopy (Crucher, 1985; Draftz, 1985). This approach was based on recommendations of the Quail Roost Conference (Stevens and Pace, 1984).

For SEM analyses reported here, a 4 $\times$ 4 mm segment of each filter was coated with carbon and placed on a SEM stage holder. The SEM operating conditions were 30-kV accelerating voltage, 100- μA beam, 26° sample tilt, and 12-mm working distance. The incident beam size was approximately 0.01 μm , but scattering and penetration caused X-rays to be emitted from a hemisphere about 1 μm in diameter. Known standards were used for SEM and EDX calibration. Each sample was scanned at low magnification to identify any non-uniform or irregular particle deposits due to sample handling. A few typical fields of view were chosen for more intensive analysis. For all particles in each field, diameters were recorded, morphologies were noted, and X-ray spectra were taken. Elements heavier than Na were detectable by EDX when their abundances exceeded about 1%. Elements lighter than Na were not detected by EDX, but if a particle was made mainly of lighter elements such as C and O in pollen or elemental carbon particles, that fact could be ascertained from the relatively low peak to background ratio and low

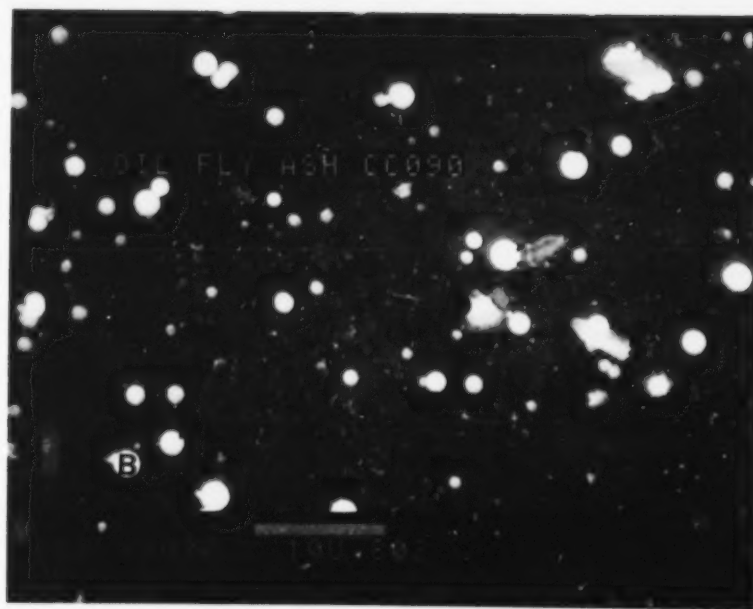
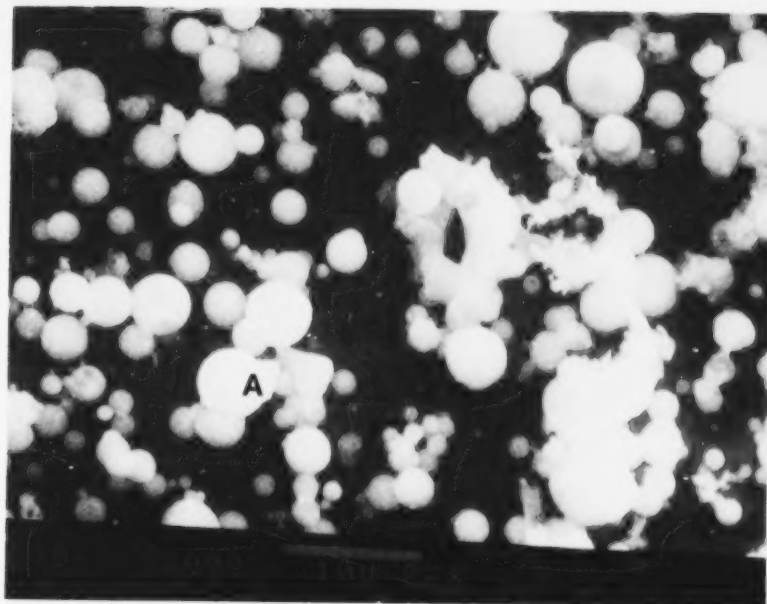
count rate for its X-ray spectrum. Examples have been reported by Mamane and Noll (1985).

The EDX spectral analysis system identified X-ray peaks and calculated their areas. The SEM-EDX system was operated manually. Although manual operation is tedious, it enabled the operator to note special particle properties and interrelationships among shape, morphology, surface features, and elemental composition. Particles were identified by shape, surface properties, inhomogeneity in appearance, and elemental content. Types of particles identified were numerous because there were several types of sources,



PHILADELPHIA AIRSHED AEROSOL STUDY, SUMMER, 1982

Fig. 1. Map showing locations of source, ambient, and soil sampling sites.



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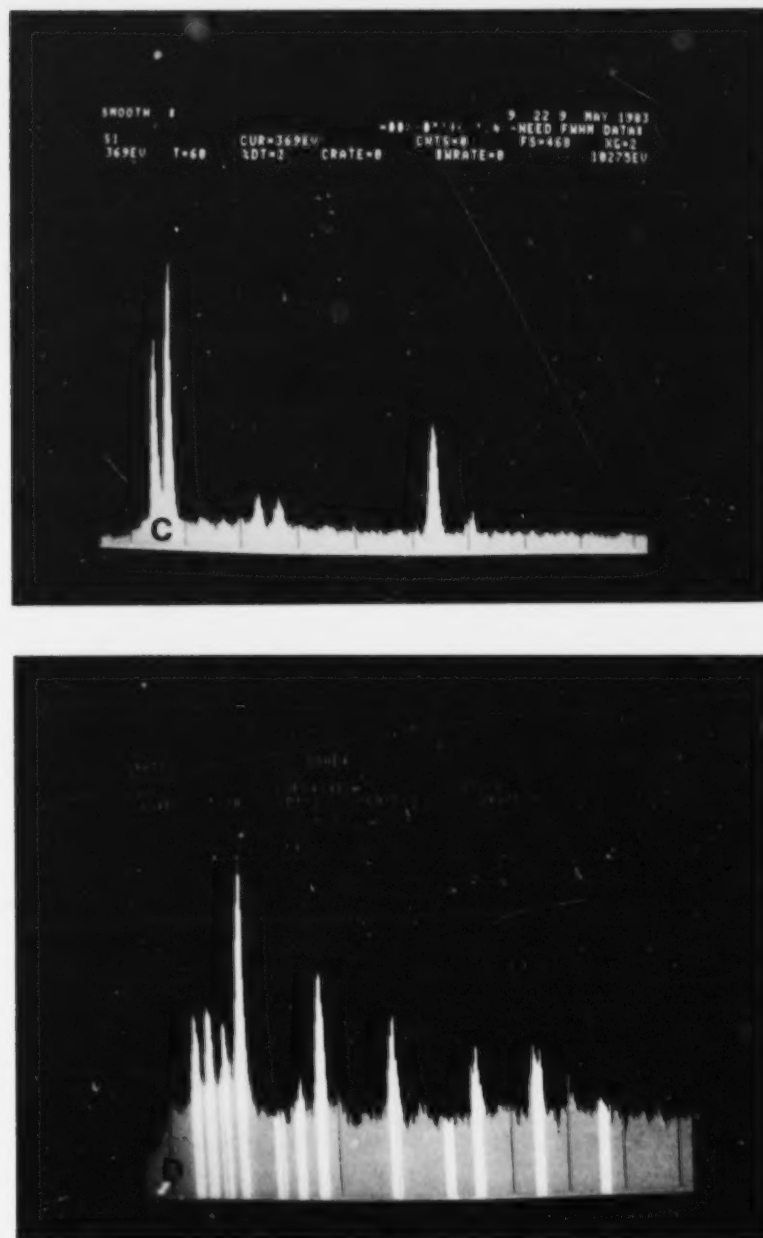


Fig. 2. Typical micrographs of (A) coal- and (B) oil-fly ash particles in the coarse fraction and typical X-ray spectra for (C) coal- and (D) oil-fly ash.

and because sources such as oil- and coal-fired power plants emit several particle types (Mamane *et al.*, 1986).

During the SEM observation, each particle was assigned to one of the following categories: (a) Biologicals – particles defined by characteristic morphology and low X-ray count rate and low peak to background ratio. They include pollen, spores, plant and animal fragments. (b) Minerals – nonspherical particles of soil origin, such as calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), quartz (SiO_2), gypsum (CaSO_4), and more complex mixtures of alkaline earth silicates containing Na, Mg, Al, Si, K, Ca, Ti, and Fe. (c) Oil fly ash – includes lacy, S-rich spheres, smooth alumino-silicate spheres which contain either V or Ni, and sulfates rich in V or Ni. (d) Coal-fly ash – includes mostly smooth spheres of alumino-silicate matrix. (e) Crustal oil-fly ash and carbonaceous oil-fly ash – identified by the presence of V or Ni in crustal spheres or sponge-like carbonaceous particles. (f) Particles of industrial origin, sulfates, elemental C and others.

3. Results and Discussion

3.1. COAL- AND OIL-FLY ASH EMISSIONS

Mamane *et al.* (1986) applied SEM-EDX to emissions from oil- and coal-fired power plants in Philadelphia. They found that over 95% of the coal-ash particles were smooth spheres containing mainly Si and Al with varying amounts of Fe, Ca, and Ti. No broken, hollow spheres were seen. Sulfur was associated mainly with the smaller size range. Figure 2a is a micrograph that illustrates the spherical morphology of coal-fly ash particles collected in the coarse fraction. Figure 2c is an X-ray spectrum of a typical coal-fly ash particle, which illustrates its crustal composition. Olmez *et al.* (1986) found that the coarse fraction collected by the dichotomous sampler accounted for > 75% of the mass of the coal-fly ash and only 7% of the mass of oil-fly ash.

Mamane *et al.* (1986) found that oil-fly ash particles has a trimodal distribution. Particles larger than 3 μm were relatively few in number and were porous or spongy, carbonaceous material rich in S, V, and Ni. Particles from 0.7 to 3 μm were mostly spheres of alumino-silicate composition some of which contained Ni or V. Particles smaller than 0.5 μm were soluble sulfates some of which contained V or Ni. Figure 2b illustrates the spherical morphology of oil-fly ash particles in the 0.7 to 3 μm size range, and Figure 2d shows the crustal element composition for a typical spherical particle in this size range. This spectrum also indicates the presence of V and Ni, which enables oil-fly ash to be distinguished from coal-fly ash. However, Mamane *et al.* (1986) found that about $35 \pm 9\%$ of the crustal spheres contained no detectable amount of either V or Ni. Therefore, our initial classification of crustal spheres into the coal- and oil-fly ash categories would cause $35 \pm 9\%$ of the crustal oil-fly ash to be classified as coal-fly ash.

3.2. SOIL PARTICLES IN THE COARSE FRACTION

Soil samples from six sites were analyzed by SEM-EDX. The sites were downtown Philadelphia (19th and Race St.), Oil City, Gulf Refineries, Philadelphia International

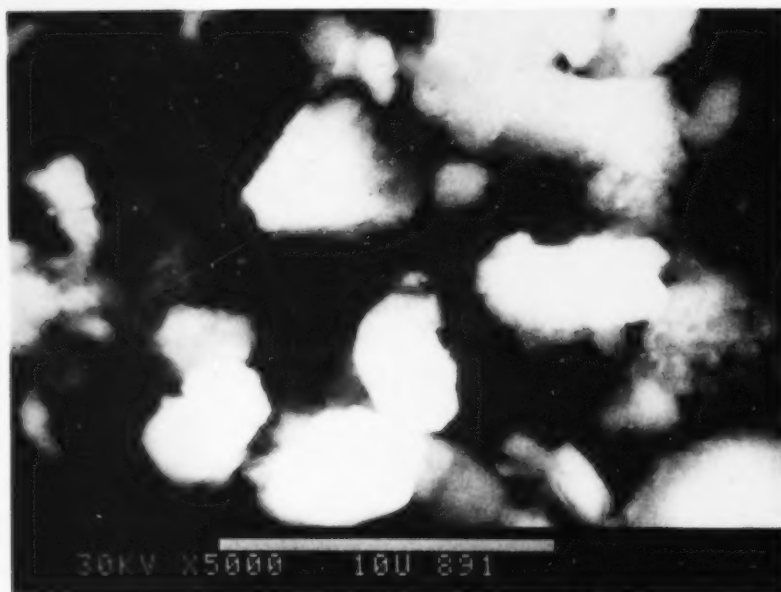


Fig. 3. A micrograph of soil particles from the Gulf Refinery site.

Airport, Gloucester City, and North Philadelphia Airport (See Figure 1). At each site 150 to 200 particles were characterized. Figure 3 is a micrograph of soil particles collected at the Gulf Refinery site, and Figure 4 shows X-ray spectra. These spectra show that large variations in Al, Si, and Fe abundances can occur among particles. Table I summarizes the soil composition by number count for the six sites. Fly ash

TABLE I

Percentage particle count by category for the coarse fraction of resuspended Philadelphia soil^a

	Downtown Phila.	Gulf Refinery	Oil City	Int. Airport	Gloucester City	North Airport
Alumino-silicates	45 ± 5	79	29	43	40	73
Quartz	40 ± 5	7	16	43	47	16
Calcite/dolomite	6 ± 2	^b	43	4	^b	^b
Gypsum	^b	^b	2	^b	^b	1
Other minerals	^b	3	^b	3	2	9
Fe-rich particles	5 ± 2	7	7	3	4	1
Coal-fly ash	2 ± 1	1	1	1	2	^b
Oil-fly ash and industrial	2 ± 1	1	2	^b	1	^b

^a Aerodynamic diameter range for coarse particles is 2.5 to 10 μ m. Typical values of precision based on counting 200 particles in a sample are shown.

^b Not detected.

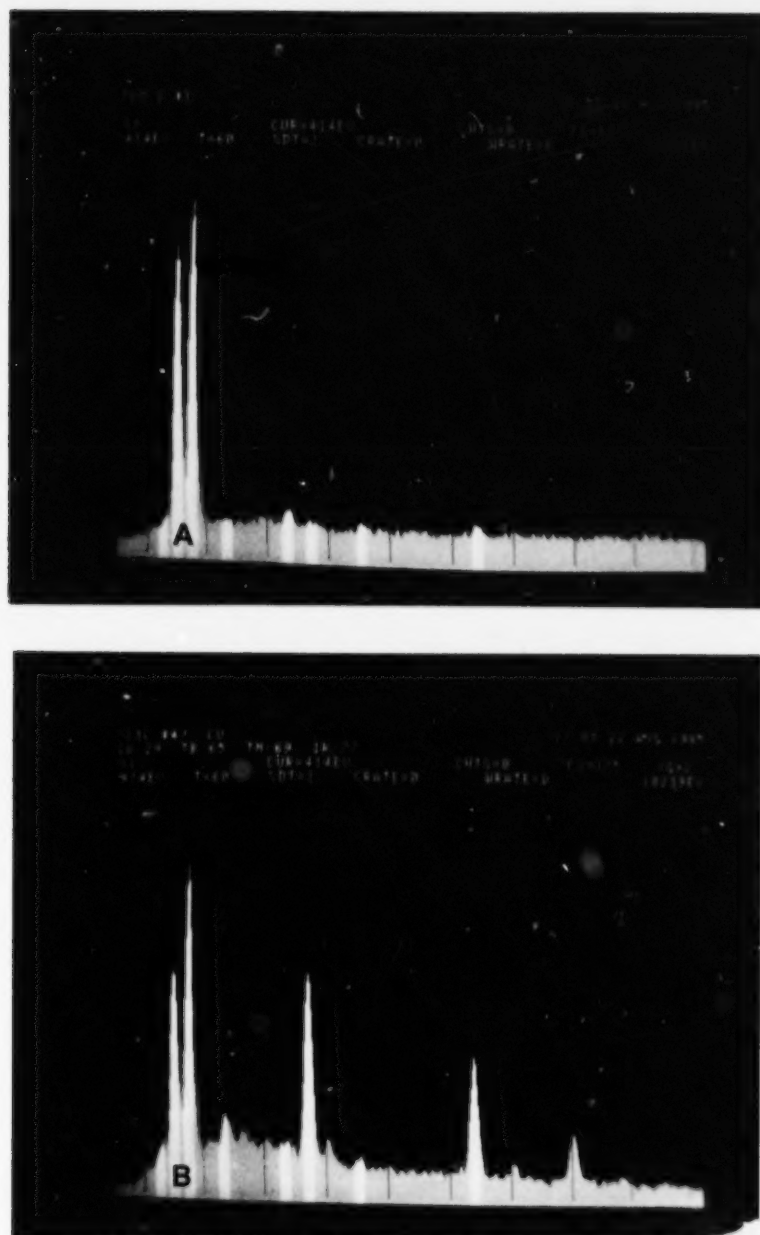
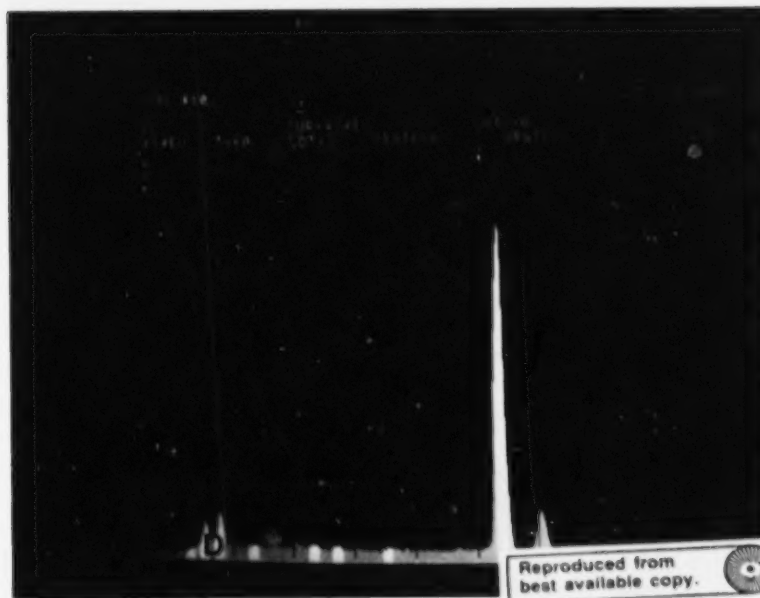
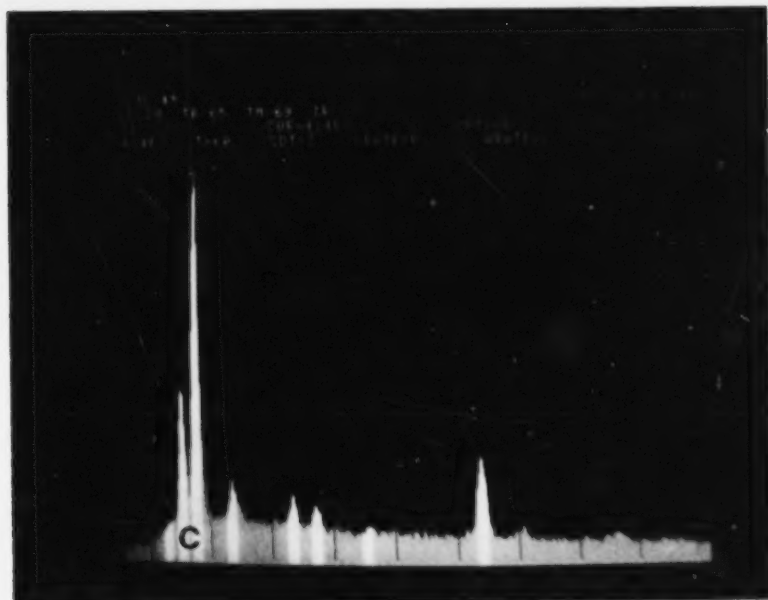


Fig. 4. X-ray spectra of particles shown in Figure 3. (A) Particle containing mainly Al and Si. (B) Particle rich in Al, Si, Ca, Fe, and Cu. (The Cu may be a contamination from the bronze heads used in the fluidized



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bed aerosol generator.) (C) Particle rich in Al, Si and Fe with small amounts of S, K, and Ca. (D) Particle rich in Fe with small amounts of Al and Si.

particles in soil ranged from 0 to 1.8%, and the area wide average was 1.1%. Differences between close sites are quite large, and it is difficult to identify an 'average, non-contaminated' soil in the Philadelphia area. The percentages given in Table I refer to particles larger than 2.5 μm aerodynamic diameter, roughly equivalent to 1.5 μm geometric diameter for crustal matter.

3.3. AMBIENT COARSE PARTICLES

Four 12-hr periods representing low, medium, and high concentrations were chosen for electron microscopy analyses. Table II shows bulk composition results by XRF and β -gauge for samples from North Airport and Camden.

TABLE II
Element and mass concentrations in ng m^{-3} measured by XRF and β -gauge for aerosol collected in the coarse (C) and fine (F) fractions*

Fraction		5 Aug., 1982 1800-0559		6 Aug., 1982 0600-1800		11 Aug., 1982 0600-1800		11 Aug., 1982 1800-0559	
		North Airport ^b	Camden	North Airport	Camden	North Airport	Camden	North Airport	Camden
Al	C	*250	425	440	670	220	300	*130	*140
Si	C	740	1900	1260	2360	590	950	86	160
S	C	230	360	230	270	53	120	52	88
K	C	92	140	130	190	80	104	40	37
Ca	C	150	300	320	220	140	260	30	53
Ti	C	29	110	*28	100	*15	31	-	*12
V	C	*2	*8	13	*10	-	-	*8	*8
Mn	C	*6	14	13	12	*1	8	-	*5
Fe	C	210	460	610	580	177	390	42	120
Cu	C	-	*3	-	-	-	34	-	-
Zn	C	32	72	9	8	26	66	30	47
Sb	C	*0	84	*4	6	*1	*2	-	-
Pb	C	53	70	28	44	16	56	15	33
Mass	C	3500	8600	10000	11900	2500	5900	300	1400
Mass	F	33800	37700	18500	17400	12100	12400	3200	13000

* (*) indicates that concentration is below three times the uncertainty.

^b Data are from a Nuclepore sample. The rest were from Teflon filter samples.

Figure 5 is a typical micrograph of particles collected on the coarse fraction filter in Camden. A variety of anthropogenic and natural particles are seen. They include minerals (Many were aggregates.), pollen and other biologicals, a smooth coal-fly ash sphere, and a lacy carbonaceous oil-ash particle. Vehicle emissions included a C chain aggregate, and a Pb-Br-Cl particle. Also identified is an organic particle with an inclusion of Fe and minerals. The small gray-appearing particles (<0.5 μm geometric dia.) are fine sulfate particles deposited on the coarse fraction filter.

Table III shows electron microscopy results for the August 5 samples from both sites. The numbers of particles counted were 150 and 195 for the North Airport and Camden,



Fig. 5. Micrograph of particles collected in the coarse fraction at Camden for the 12-hr period beginning at 1800, August 5, 1982. The following abbreviations are used: Ash - Coal-fly ash; Oil-oil-fly ash; B-botanical matter; Fe-organic material with an inclusion of Fe; EC-chain agglomerate of carbonaceous particles; M-mineral; Pb-particle rich in Pb, Br and Cl.

respectively. Minerals and biologicals accounted for 80 to 85% of the coarse particles counted at the two sites. The rest were particles of industrial origin. In all samples analyzed, about 100 fly ash spheres were detected, but none contained detectable amounts of V or Ni. Thus, we conclude that the observed crustal spheres were from coal burning rather than oil burning. However, as Table III indicates, a few carbonaceous oil-fly ash particles were observed.

Particles were classified by category and sorted into the size ranges shown in Table III. Mass concentrations were estimated for each class of particles from the following data: number of particles in each size range, effective diameter for each size range, an assumed density, fraction of filter area scanned, and air volume sampled. Particle volumes were calculated assuming they were spheres. Density was based on the assigned category and the assumption of no internal void spaces. Here we do not report results for chain aggregates containing C, Br, and Pb, which could contain void spaces. Although large fly ash spheres are often hollow, Fisher *et al.* (1978) showed that most small ones ($<4 \mu\text{m}$) are solid spheres. Thus, the density of coal-fly ash will be similar to that of the original silicate- and Ca-rich minerals in coal. Densities of typical silicate minerals such as quartz, feldspar and kaolinite are 2.65, 2.57, and 2.6–2.65 g cm^{-3} , respectively. Densities of typical Ca-rich minerals such as gypsum, calcite, and dolomite

TABLE III
Particle count by category vs diameter range in $\mu\text{m}^{\text{a,b}}$

	North Airport					Camden				
	<1.5	<2.1	<3.1	<5.1	<10	<1.5	<2.1	<3.1	<5.1	<10
Minerals:										
Silicates	3	15	18	6	1	7	22	9	6	3
Quartz		8	3	3	1		6	3	3	
Ca-rich	1	4	2			2	5	5	2	1
Others		1				1	5	5		
Bioglogicals	1	10	25	20	4	1	16	19	21	7
Fly ash:										
Crustal ash						3	3			
C-rich oil					1					1
Industrial/ commercial:										
Organics	1	7	2		1	3	5	6	3	
Fe-rich	4	1		1		3	2	2		
Pb-rich	2	1	1			1	3	2	1	
Zn-rich							1		1	
Sb-rich							1	1		
Others	1	1			1	2	1			

^a Coarse fraction 12-hr sample that began on August 5, 1982 at 1800 EDT.

^b Biologicals include spores, pollen, and plant and animal fragments.

are 2.32, 2.71, and 2.85 g cm^{-3} , respectively. Thus, a density of $2.6 \pm 0.4 \text{ g cm}^{-3}$ is appropriate for most crustal particles collected in our study. Accuracy for mass concentration was estimated to be 30 to 40% and was based on uncertainty in density, uncertainty in estimating particle volume, and counting statistics.

TABLE IV
Coarse fraction fly ash, mineral, and crustal matter mass concentrations in $\mu\text{g m}^{-3}$ based on SEM-EDX, XRF, and β -gauge analyses

Method		North Airport				Camden			
		Aug. 5-6 night	Aug. 6 day	Aug. 11 day	Aug. 11-12 night	Aug. 5-6 night	Aug. 6 day	Aug. 11 day	Aug. 11-12 night
Crustal fly ash	SEM-EDX	0.0	0.16	0.18	0.08	0.04	0.32	0.15	0.08
Minerals	SEM-EDX	3.8	3.8	1.6	0.4	5.3	5.8	2.9	1.1
Crustal matter ^a	SEM-EDX	3.8	4.0	1.8	0.5	5.3	6.1	3.1	1.2
Crustal matter ^b	XRF	2.7	4.9	2.2	0.5	6.6	8.1	3.6	0.79
Total mass	β -gauge	3.5	10.0	2.5	0.3	8.6	11.9	5.9	1.4

^a Crustal matter determined by SEM-EDX is the sum of coal fly ash and minerals. Estimated accuracy is ± 30 to 40%.

^b Crustal matter from XRF data was computed as the sum of O, Al, Si, K, Ca, Fe, and Ti, where the O abundance was assumed to be 1.7 times that of Si. Estimated accuracy is $\pm 15\%$.

Table IV lists estimates of mass concentrations of fly ash, minerals, and crustal matter for both sites during four sampling periods based on electron microscopy calculations. Here crustal matter refers to the sum of fly ash and minerals. Crustal fly ash values range from 0 to 180 ng m^{-3} at North Airport and 40 to 320 ng m^{-3} at Camden. Crustal fly ash concentrations varied substantially from day to day, but the variations between sites on any given day were somewhat smaller. This is consistent with fly ash particles being emitted from multiple elevated sources, which enables them to spread somewhat uniformly over the metropolitan area. The average ratio of crustal fly ash to crustal matter was 8 (4)% and 4 (1)% (standard error in parentheses) at North Airport and Camden, respectively. The soil samples also contained fly ash, but the average amount was only 1 (1)%. Therefore, <25% of the fly ash in the atmosphere could be attributed to suspension of soil.

Table IV also lists XRF results for crustal matter expressed as the sum of O, Al, Si, K, Ca, Ti, and Fe. The O abundance was assumed to be 1.7 times that of Si because the factor 1.7 represents the O to Si ratio in the earth's crust. Table IV indicates that the XRF and SEM-EDX results for the total crustal matter agree within the estimated accuracy. The ratio of SEM to XRF data ranges from 0.75 to 1.5 and the mean ratio

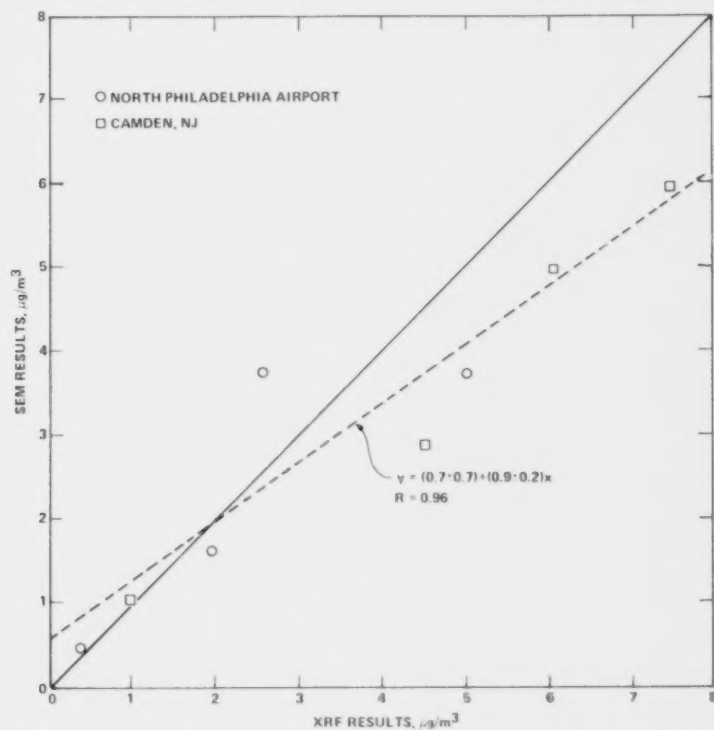


Fig. 6. Comparison of crustal matter concentrations deduced from SEM and XRF data.

(and standard deviation) is 1.0 (0.3) for the eight pairs of results. Figure 6 is a plot of the total mineral concentration from SEM analysis versus the XRF mineral data. The correlation coefficient is 0.96.

3.4. AMBIENT FINE PARTICLES

Six fine fraction samples were analyzed by SEM-EDX. For each sample, 10 to 30 fields of view at 5000 magnification were scanned. Table V summarizes concentrations of fly ash and minerals based on microscopy. Crustal fly ash concentrations ranged from 6 to 75 ng m^{-3} , and mineral concentrations ranged from 30 to almost 300 ng m^{-3} . Fly ash accounted for 7 to 60% of the crustal matter and 0.05 to 2.3% of the fine aerosol mass concentration. Figures 7a and 7b are typical micrographs of samples from Camden on August 5-6 (night) and August 11-12 (night). They represent samples of high and low loading of sulfur (See XRF data in Table V). Most particles in both samples were droplet like and gray in appearance, and only S was detected by EDX. We assumed they were mixtures of ammonium sulfate and sulfuric acid. The brighter particles were not sulfate but were elemental C (large agglomerate in the middle of Figure 7a), spores (sphere on the right side of Figure 7b), and a few particles of industrial sources and power plants.

Crustal matter concentrations deduced by SEM-EDX are about a factor of 4 lower than those based on XRF (see Table V). A likely cause is that the high loading of sulfate particles may mask some of the minerals causing them not be detected by SEM. Also,

TABLE V
Fine fraction species concentrations in ng m^{-3} based on SEM-EDX, XRF, and β -gauge analyses

		Aug. 5-6 1800-0600		Aug. 11 0600-1800		Aug. 11-12 1800-0600	
		North Airport	Camden	North Airport	Camden	North Airport	Camden
Fly ash	SEM	21 $\pm$ 8	21	30	6	75	9
Minerals	SEM	283 $\pm$ 110	207	87	152	47	29
Crustal	SEM	304 $\pm$ 120	228	117	158	122	38
Crustal	XRF	1000 $\pm$ 150	1100	440	510	210	270
Al	XRF	73 $\pm$ 110	nd	71	87	nd	61
Si	XRF	240 $\pm$ 21	270	90	90	42	31
S	XRF	5500 $\pm$ 400	5900	1800	1900	1500	1700
K	XRF	110 $\pm$ 8	130	25	40	41	46
Ca	XRF	52 $\pm$ 6	60	23	29	17	20
Ti	XRF	18 $\pm$ 9	26	11	nd	nd	nd
Fe	XRF	110 $\pm$ 8	120	62	110	36	57
Zn	XRF	110 $\pm$ 7	200	105	75	210	160
Br	XRF	29 $\pm$ 2	110	16	20	18	30
Pb	XRF	280 $\pm$ 16	300	94	180	115	160
Se	XRF	1.5 $\pm$ 0.6	nd	0.5	0.7	0.5	1.2
Mass	β -gauge	33800 $\pm$ 3100	37700	12100	12400	3200	13000

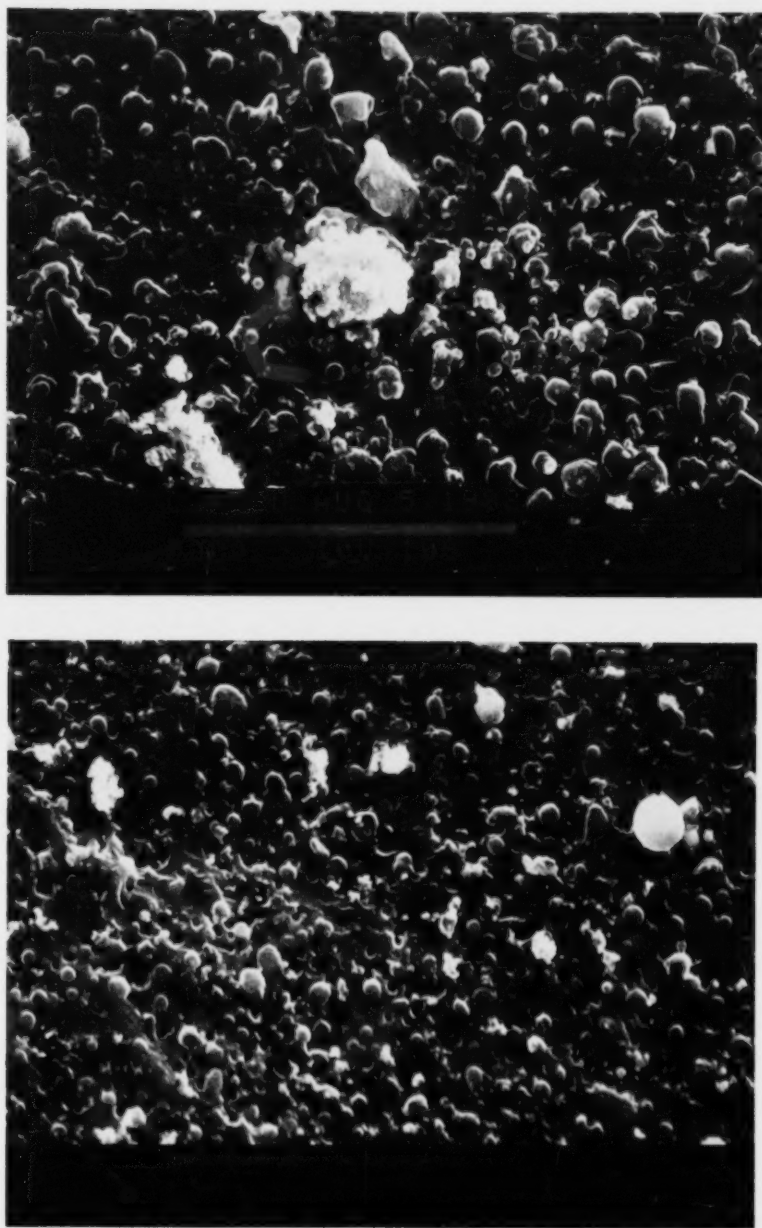


Fig. 7. Micrographs of fine particles collected at night on (A) August 5-6 and (B) August 11-12.

some of the Al, Si, K, Ca, Ti, and Fe measured by XRF may not be in the form of minerals, which would cause us to overestimate the mineral content of the fine fraction. For example, K was often associated with biological particles.

4. Summary and Conclusions

Eight samples of ambient aerosols at two sites in the Philadelphia area were analyzed by scanning electron microscopy and energy dispersive X-ray analysis to determine fly ash concentrations and the ratio of fly ash to mineral concentrations. Six soil samples representing different land uses and samples from oil- and coal-fired power plants were also analyzed. The use of SEM-EDX was able to resolve fly ash and minerals making that technique a very valuable complement to the application of the chemical mass balance method applied to XRF data. Although fly ash spheres were detected in soil, their abundance was low suggesting that resuspended soil could account for no more than 25% of atmospheric fly ash.

In all cases, mineral particles and biologicals dominated the coarse fraction of ambient aerosol. Industrial and commercial activities contributed 20 to 40% by number concentration in Camden, and 15 to 30% in the North Airport site. The industrial and commercial activities include oil- and coal-fired power plants, steel industries, antimony roasting, incinerators, and motor vehicles. Fly ash concentration deduced for the eight cases ranged from 0 to 320 ng m^{-3} while the mineral material contributed from 400 to 5800 ng m^{-3} . Crustal matter concentrations calculated from X-ray fluorescence elemental data agreed with results based on electron microscopy within the estimated 30 to 40% errors for microscopy computations.

Sulfate particles dominated the fine fraction, but a small amount of crustal particles, 40 to 300 ng m^{-3} was detected. Coal-fly ash concentrations ranged from 6 to 75 ng m^{-3} ; no oil-fly ash was detected in the fine fraction.

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